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USE OF STRUCTURE–REACTIVITY RELATIONSHIPS TO ESTIMATE HYDROLYTIC PERSISTENCE OF CARBAMATE PESTICIDES

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Abstract—Linear free energy relationships are given for use in estimating alkaline hydrolysis of carbamate pesticides in water as applied to environmental conditions. Plots of the second-order alkaline hydrolysis rate constants versus pK_a of the resulting alcohol are given for *N,N*-dimethyl-, *N*-methyl-*N*-phenyl-, *N*-methyl-, and *N*-phenyl-carbamates. Use of these relationships allows one to estimate rate constants for specific compounds and make general statements about hydrolytic stability of classes of compounds.

INTRODUCTION

Several papers have appeared in the environmental literature dealing with the hydrolysis of carbamate pesticides (Aly & El-Dib, 1971; Wolfe *et al.*, 1978). In a recent review article, Faust & Gomaa (1972) suggested that carbamates hydrolyze slowly in water and, therefore, might be more persistent in natural waters than commonly believed.

Wolfe *et al.* (1978) showed that the alkaline hydrolysis half-life for two commonly used carbamate pesticides varies dramatically with structure. For example at pH 9 and 27°C, the half-life for carbaryl is 0.15 days; whereas, for propham it is greater than 1×10^4 days. This five-orders-of-magnitude variation in hydrolytic activity with variation of substituents raises the question of what structural features enhance the hydrolytic breakdown of carbamates in an aquatic environment. This paper deals with the use of structure reactivity relationships in predicting hydrolysis half-lives for the numerous carbamate pesticides now being applied widely in the environment. Williams (1973) has previously examined the structure reactivity relationship for some *N*-phenyl carbamates; we have extended the study to include carbamates used as environmental agents including *N*-monoalkyl and *N,N*-dialkyl substituted compounds.

DISCUSSION

An examination of the pesticide literature indicates that *N*-methyl, *N,N*-dimethyl, *N*-phenyl, and *N*-phenyl-*N*-methyl carbamates represent most of the carbamates used as environmental agents (Melnikov, 1971). Although carbamates have been reported to undergo acid catalyzed, neutral, and alkaline hydrolysis, only alkaline hydrolysis is likely to occur at pH's and temperature common to the aquatic environment. The mechanism of carbamate alkaline hydrolysis has been characterized by several groups of investigators (Aly & El-Dib, 1971; Dittert & Higuchi, 1963; Williams, 1972; Williams, 1973; Bender & Homer, 1965). It appears that two different mechanisms are operative with the distinguishing structural feature being *N*-mono- or *N,N*-di-substitution. Because the isolatable products are the alcohol and the amine in either pathway, the environmental significance lies in the quantitative effect substituents have on the rate of reaction in each of the two mechanisms.

Carbaryl, a commonly used pesticide, is an example of a *N*-substituted carbamate that is believed to hydrolyze as shown in Fig. 1 (Vontor *et al.*, 1972). In this mechanism, an acid-base equilibrium is established and the conjugate base of the carbamate undergoes an elimination type reaction to give the unstable carbamic acid that decomposes to the primary amine and carbon dioxide.

On the other hand, the *N,N*-disubstituted analog undergoes hydrolysis by a mechanism similar to that of carboxylic acid esters, that is, by going through a tetrahedral intermediate (Fig. 2). The transient isocyanate intermediate breaks down via carbamic acid to give the primary amine and carbon dioxide.

The use of free energy relationships to estimate alkaline hydrolysis rate constants should be useful in predicting hydrolytic stability of these pesticides in aquatic ecosystems. One such structural reactivity correlation is that between the second-order-alkaline hydrolysis rate constants (k_2) and the pK_a of the resulting alcohols formed upon hydrolysis (Hammett, 1970). Although the rate constants have been correlated successfully using other relationships, it is probably more convenient to use pK_a's because these data are more readily available to environmentalists (Williams, 1973; Kortum *et al.*, 1961).

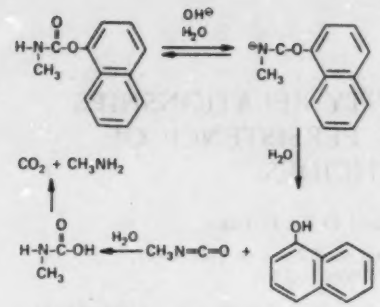

Fig. 1. Mechanism for the alkaline hydrolysis of the *N*-alkyl substituted carbamate, carbaryl.

Linear free energy relationships

(1) N-*Phenyl and* N-*methyl*-N-*phenyl carbamates.* Plots of the log of the second-order alkaline hydrolysis rate constants versus the pK_a of the resulting alcohol are given in Fig. 3 for some selected *N*-substituted phenyl and *N*-methyl-*N*-substituted phenyl carbamates (Casida *et al.*,1960; Christenson, 1964; Kukuto *et al.*, 1967; Williams, 1973; Wolfe *et al.*, 1977). This plot was constructed using data from the pesticide literature and that of Williams (1973). The equation for the line is given by

$$\log k_2 = \rho \log K_a + C$$

where log k_2 refers to the second-order alkaline hydrolysis rate constant; ρ, the slope of the line, is a measure of the sensitivity of the reaction rate to changes in the alcohol moiety; K_a is the ionization constant for the resulting alcohol; and C is the intercept of the line. For *N*-methyl-*N*-phenyl carbamates, p is -0.26 ± 0.001 ($C = -1.3 \pm 0.1$); whereas for *N*-phenylcarbamates, ρ is -1.15 ± 0.02 ($C = 13.6 \pm 0.2$). A change in the alcohol moiety for the *N*-phenyl carbamates has a pronounced effect on the hydrolysis rate.

The plots in Fig. 3 can be used to calculate hydrolysis rate constants for new and existing carbamate pesticides provided the pK_a of the alcohol is known or can be estimated. In the case of *N*-methyl-*N*-phenyl carbamates, however, it is not likely that chemical hydrolysis will be fast enough to be important under most environmental conditions. For example, even in the extreme case for an alcohol of pK_a of 1 (i.e. picric acid), the half-life would be 5 yr at pH 8.

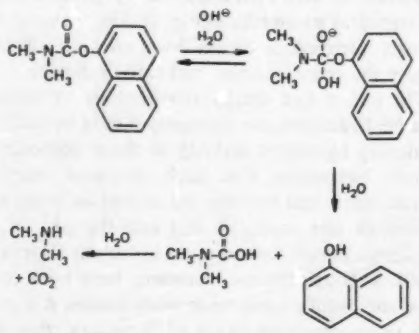

Fig. 2. Mechanism for the alkaline hydrolysis of the *N*,*N*-dialkyl carbamate, 1-naphthyl *N*,*N*-dimethylcarbamate.

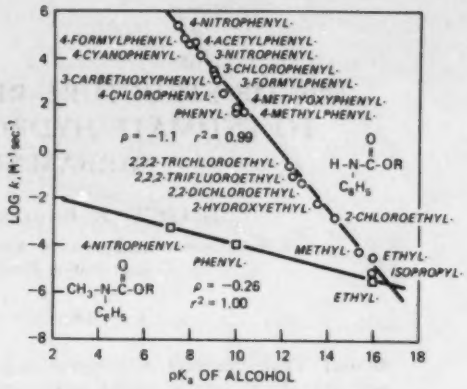

Fig. 3. Plots of the second-order alkaline hydrolysis rate constants of *N*-phenyl carbamates versus pK_a of the resulting alcohol at 25°C in water.

On the other hand, the *N*-phenyl carbamates, which are more reactive and more sensitive to changes in alcohol structure, may readily hydrolyze. When the resulting alcohol has a pK_a of less than 12, the chemical hydrolysis half-life at pH 8 and 25°C will be less than six months. In this situation, hydrolysis should be considered as a viable degradation pathway in the aquatic environment.

In general, it appears that most carbamates made with aliphatic alcohols generally would not hydrolyze under environmental conditions. The compounds comprised of aryl alcohols may hydrolyze at a significant rate, however, depending on the aryl moiety and the substituents.

(2) N-*Methyl and* N,N-*dimethyl carbamates.* Similar Plots are given in Fig. 4 for *N*-methyl and *N*,*N*-

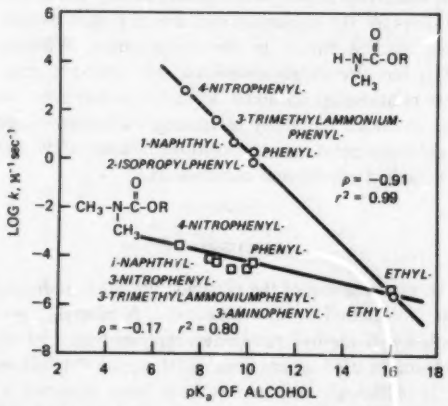

Fig. 4. Plots of the second-order alkaline hydrolysis rate constant of the *N*-alkyl carbamates versus pK_a of the resulting alcohol at 25°C in water.

dimethyl carbamates (Casida *et al.*, 1960; Christenson, 1964; Fukuto *et al.*, 1967). In the case of *N,N*-dimethyl carbamates, the reaction is fairly insensitive to the structural features of the alcohol ($\rho = -0.17 \pm 0.04$; $C = -2.6 \pm 0.4$). Based on this plot, it is unlikely that any of the *N,N*-dimethyl carbamates would hydrolyze under environmental conditions. The *N*-methyl carbamates, however, are more reactive and also more sensitive to structural changes of the alcohol as shown by a ρ value of -0.91 ± 0.03 ($C = 9.3 \pm 0.4$). When the resulting alcohol has a pK_a of 10 or larger, the chemical hydrolysis half-life will be six months or greater at pH 8 and 25°C.

(3) *Effect of other* N-*substituents.* So far, only *N*-methyl and *N*-phenyl mono- and disubstituents have been considered. Ideally, one would obtain a family of lines as the *N*-substituents were varied for a series of alcohols. Unfortunately, enough data are not available to construct these families of lines, but general statements can be made as to how the variance of *N*-substituents will affect hydrolysis. In the case of *N,N*-dialkyl substitution, hydrolysis is not likely to be important. For *N*-alkyl-*N*-aryl compounds, hydrolysis will be slow except when the aryl moiety contains electron withdrawing groups.

SUMMARY

Based on these free energy plots, it is apparent that many carbamate pesticides will not readily hydrolyze in natural waters. Only in the case of *N*-substituted carbamates for which the resulting alcohols have pK_a's less than 12 will hydrolysis likely be fast enough to be an important degradation pathway. Thus, kinetic studies of other pathways must be considered in evaluating the fate of many carbamates in aquatic ecosystems.

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